

THERMODYNAMIC STUDY OF METAL SULPHIDES CONVERSION TO OXIDES IN HYDROMETALLURGY

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This paper presents thermodynamic study of the conversion of metal sulphides to oxides of the CuAg sulphide concentrate as a final product after mechano-chemical leaching of tetrahedrite. The conversion of sulphides to oxides is carried out by oxidation leaching in NaOH solution. The thermodynamic calculation was performed for the sulphide concentrate containing the following sulphides: CuS, CuFeS₂, FeS, Sb₂S₃, As₂S₃, Bi₂S₃ and HgS. Based on the change of Gibbs free energy (ΔG°) and the equilibrium constant (K), conversion of metal sulphides to oxides from the qualitative assessment of the chemical reaction can occur as the result of the thermodynamic reaction abilities.

Key words: hydrometallurgy, sulphide, thermodynamic analysis, leaching, conversion

INTRODUCTION

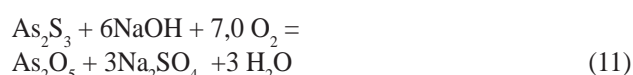
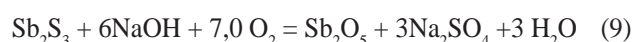
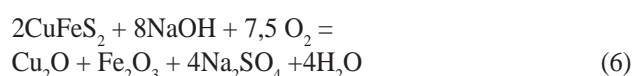
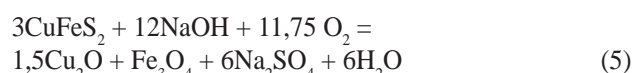
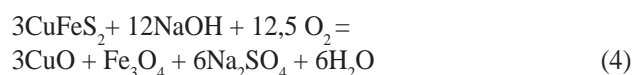
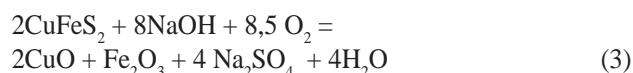
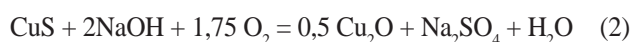
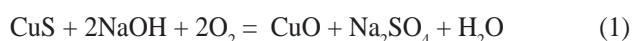
The thermodynamic study of the conversion of metal sulphides into oxides is applied to the hydrometallurgical processing of the tetrahedrite concentrate. Laboratory investigations were performed with tetrahedrite concentrate from Mária-Rožnava mine in Slovakia having the chemical composition of 21 % Cu, 11 % Sb, 28 % S, 1 % As, 2 % Zn, 0,2 % Ag and 1 % Hg. X-ray analysis reveal following proportions of dominating phases: 41 % Tetrahedrite (Cu₄Sb₄S₁₃), 12 % Chalcopyrite (CuFeS₂) and 25 % Pyrite (FeS₂) [1-4].

EXPERIMENTAL PART

The relationship between thermodynamic efficiency of the conversion of metal sulphides to oxides and initial values of NaOH and O₂ was calculated using the HSC Chemistry software based on the equilibrium composition of reactants and reaction products used as inputs for the calculation [5-10]. The evaluated equilibrium compositions and thermodynamic efficiency characterize the quantitative part of chemical reactions. Thus, it is possible to consider quantitative chemical thermodynamics [11].

The conversion of metal sulphides was also examined when developing technological projects [12-13].

Thermodynamic efficiency of the conversion of metal sulphide to oxide was calculated for the following chemical reactions:



The values for thermodynamic probability of the chemical reaction processes (1) ÷ (15) under standard conditions depending on ΔG° and K value are given in Table 1.

Thermodynamic probability of the conversion of metal sulphides to oxides under standard conditions decreases from $\text{HgS} \rightarrow \text{HgO}$, eq. (15) to $\text{CuFeS}_2 \rightarrow \text{CuO}$

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+ Fe_3O_4 , eq. (4) in the order listed in Table 1. The contents of sulphide tetrahedrite concentrate (solid phase following the mechano-chemical leaching) for calculation of the equilibrium composition are given in Table 2. These products are Cu, Fe sulphide concentrate where the impurities present are Sb, As, Bi and Hg.

Na_2SO_4 is formed in the solution after the conversion of metal sulphides to oxides.

Using CsO or BaO it is possible to salt out sodium sulphate from the solution to form CaSO_4 or BaSO_4 in the solid phase and, thus, to assess sulphur.

The above-mentioned reactions (17), (18) are thermodynamically feasible; the reaction with BaO in comparison to CaO is thermodynamically more favorable and is largely shifted towards the formation of products. Obtaining sulphur with the help of MgO is not feasible (19). Sodium hydroxide that is formed in the reactions (17), (18) is recyclable to oxide leaching of metal sulphides when converted to oxides – reactions (1) ÷ (16).

Table 1 **Thermodynamic probability of metal sulphide conversion to oxides depending on ΔG° and K at $t = 60^\circ\text{C}$**

Conversion	$\Delta G^\circ / \text{kJ}$	K	Eq. no.
$\text{HgS} \rightarrow \text{HgO}$	- 668,9	$7,8\text{E} + 104$	15
$\text{CuS} \rightarrow \text{Cu}_2\text{O}$	- 755,0	$2,5\text{E} + 118$	2
$\text{CuS} \rightarrow \text{CuO}$	- 807,3	$3,9\text{E} + 126$	1
$\text{FeS} \rightarrow \text{Fe}_3\text{O}_4$	- 971,5	$2,2\text{E} + 152$	8
$\text{FeS} \rightarrow \text{Fe}_2\text{O}_3$	- 1 846,7	$3,7\text{E} + 289$	7
$\text{Bi}_2\text{S}_3 \rightarrow \text{BiO}$	- 2 211,2	$1,0\text{E} + 308$	13
$\text{Bi}_2\text{S}_3 \rightarrow \text{Bi}_2\text{O}_3$	- 2 321	$1,0\text{E} + 308$	14
$\text{Sb}_2\text{S}_3 \rightarrow \text{Sb}_2\text{O}_3$	- 2 461,2	$1,0\text{E} + 308$	10
$\text{As}_2\text{S}_3 \rightarrow \text{As}_2\text{O}_3$	- 2 466,0	$1,0\text{E} + 308$	12
$\text{Sb}_2\text{S}_3 \rightarrow \text{Sb}_2\text{O}_5$	- 2 649,0	$1,0\text{E} + 308$	9
$\text{As}_2\text{S}_3 \rightarrow \text{As}_2\text{O}_5$	- 2 663,8	$1,0\text{E} + 308$	11
$\text{CuFeS}_2 \rightarrow \text{Cu}_2\text{O} + \text{Fe}_2\text{O}_3$	- 3 133,0	$1,0\text{E} + 308$	6
$\text{CuFeS}_2 \rightarrow \text{CuO} + \text{Fe}_2\text{O}_3$	- 3 237,0	$1,0\text{E} + 308$	3
$\text{CuFeS}_2 \rightarrow \text{Cu}_2\text{O} + \text{Fe}_3\text{O}_4$	- 4 635,8	$1,0\text{E} + 308$	5
$\text{CuFeS}_2 \text{ v } \text{CuO} + \text{Fe}_3\text{O}_4$	- 4 792,5	$1,0\text{E} + 308$	4

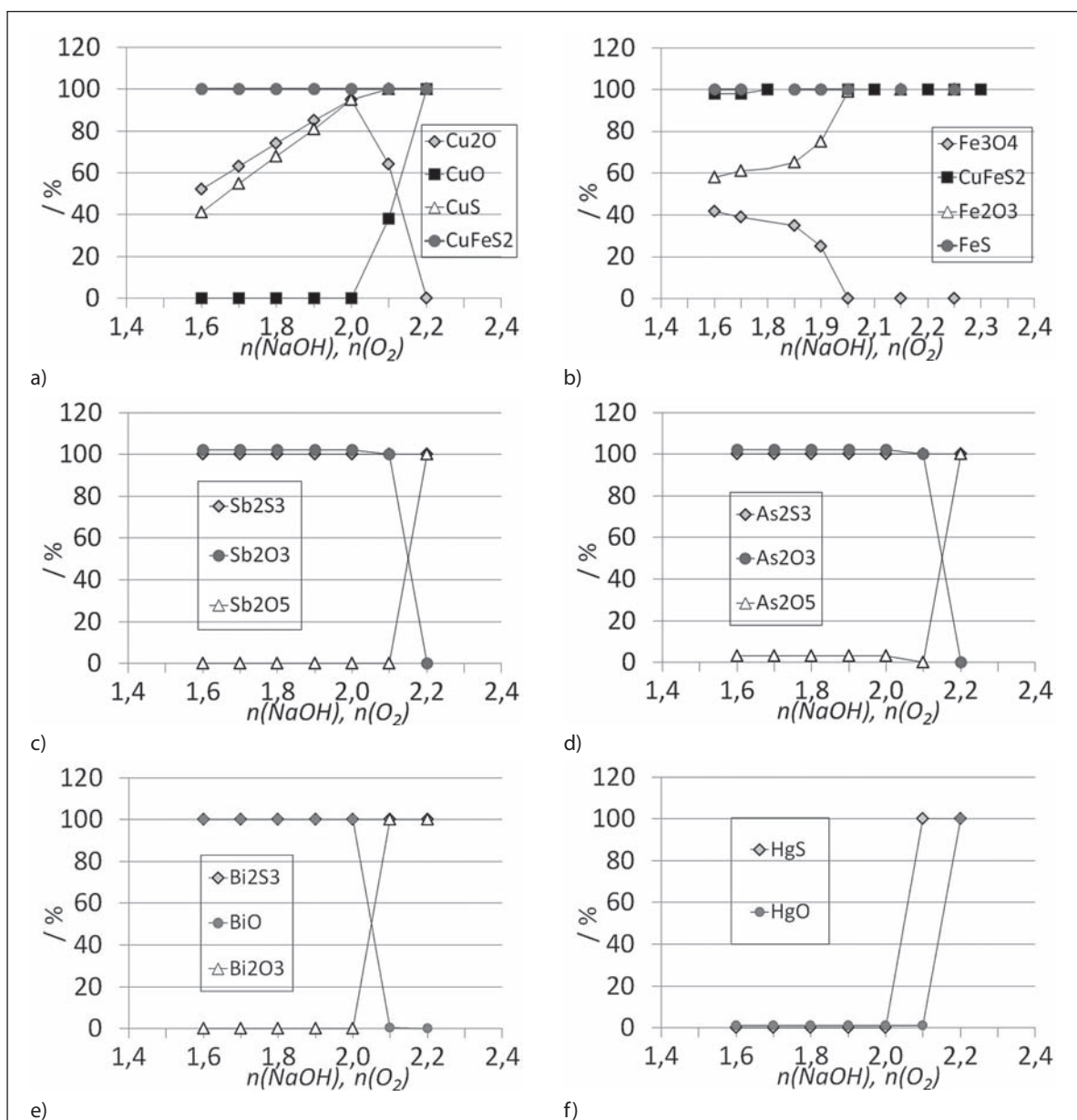


Figure 1 Thermodynamic efficiency of the conversion of metal sulphide to oxide and formation of metal oxide as a reaction product compared to initial weights of NaOH and O_2 : a – Cu, b – Fe, c – Sb, d – As, e – Bi, f – Hg

Table 2 Composition of sulphide concentrate / wt. %

CuS	41,62
CuFeS ₂	14,78
FeS	36,03
Sb ₂ S ₃	1,13
As ₂ S ₃	0,82
Bi ₂ S ₃	0,53
HgS	0,05
spoil	5,04

Calculation of the equilibrium composition in accordance with [1] was carried out under the following conditions: $m_{conc} = 100$ g, $t = 60$ °C, $p = 0,1$ MPa. The initial and equilibrium values of the conversion of metal sulphide to oxide for $n_{NaOH} = n_{O_2} = 1,6 \div 2,2$ mol are shown in Figure 1a - 1f.

RESULTS AND DISCUSSION

ΔG° and K values listed in Table 1 show that from the given sulphides the conversion $HgS \rightarrow HgO$ and $CuS \rightarrow Cu_2O$ is the least probable. The agents NaOH and O_2 in the amount lower than stoichiometric ($< 2,06$ mol and $< 2,19$ mol for NaOH and O_2) allow conversion of CuS to Cu_2O and CuO (Figure 1). Stoichiometric amounts of NaOH and O_2 for the conversion of metal sulphides to oxides are given in Table 3.

Table 3 Stoichiometric amounts of NaOH and O_2 for the conversion of metal sulphides to oxides

Metal sulphides	m_{NaOH} / g	m_{O_2} / g
CuS	34,820	27,860
CuFeS ₂	12,886	10,950
FeS	32,787	29,510
Sb ₂ S ₃	0,798	0,745
As ₂ S ₃	0,799	0,746
Bi ₂ S ₃	0,247	0,198
HgS	0,016	0,012
Σg	82,353	70,022

Stoichiometric amounts of NaOH and O_2 were calculated on assumption that CuO, Fe_2O_3 , Sb_2O_5 , As_2O_5 , Bi_2O_3 , and HgO were formed in the conversion of metal sulphides to oxides CuO, Fe_2O_3 , Sb_2O_5 , As_2O_5 , Bi_2O_3 , and HgO were formed. The total stoichiometric amount of NaOH and O_2 , for all the sulphides converted to oxides is 82,353 g. The amounts of NaOH and O_2 , which react in relation to their initial amount, are given in Table 4.

When the initial amount of NaOH is 1,6 mol, only 62,48 g of NaOH is at the disposal. Probability of thermodynamic capacity for the conversion $CuS \rightarrow Cu_2O$ given by ΔG° and K values allows concluding that all metal sulphides convert to metal oxides before HgS and CuS. Table 3 shows that 34,836 g of NaOH is required for the conversion of HgS and CuS.

When this stoichiometric value is subtracted from the total stoichiometric value ($82,353 - 34,836 = 47,517$ g), the result expresses the amount of NaOH required for the conversion of all other mentioned sulphides.

Table 4 The amounts of NaOH and O_2 entering reactions in relation to their respective initial amounts

Original amount of NaOH, O_2 / mol	Reacted amount			
	NaOH		O_2	
	/ mol	/ g	/ mol	/ g
1,6	1,562	62,48	1,6	51,2
1,7	1,675	66,99	1,7	54,4
1,8	1,787	71,48	1,8	57,6
1,9	1,897	75,88	1,9	60,8
2,0	1,999	79,96	2,0	64,0
2,1	2,059	82,35	2,1	67,2
2,2	2,059	82,35	2,19	70,08

When the value (34,836) is subtracted from the amount of NaOH to be at the disposal in the original state, i.e. 1,6 mol (62,48 g), see Table 4, the result gives the value of NaOH left for CuS conversion ($62,48 - 47,517 = 14,963$ g). The amount 14,963 g of NaOH is sufficient for converting 42,96 % CuS only. This is in the agreement with the value of thermodynamic efficiency of CuS conversion to oxides for 1,6 mol of NaOH, the value of 43 % in Figure 1a. The values given in Figures 1a - 1f were calculated on the basis of equilibrium values using HSC Chemistry software [1] and a method according to [2]. All other sulphides except for HgS and CuS convert to oxides totally, practically with 100 % thermodynamic efficiency from the very beginning at original values $n_{NaOH} = n_{O_2} = 1,6$ mol. In relation to the original NaOH and O_2 values the oxides with lower valence are formed. Oxides Cu_2O and BiO are formed at original values from 1,6 to 2,0 mol (Figure 1a, 1e). From 1,6 to 2,1 mol, oxides Sb_2O_3 and As_2O_3 are formed (Figure 1c, 1d). Very interesting are FeS and CuFeS₂ conversions, when besides Fe_3O_4 also Fe_2O_3 is formed at original values from 1,6 to 2,0 mol (Figure 1b). At original NaOH and O_2 values above 2,0 mol only oxides HgO, CuO, Bi_2O_3 and Fe_2O_3 are formed. Above 2,1 mol oxides Sb_2O_5 and As_2O_5 are formed.

CONCLUSIONS

- Qualitative evaluation of the chemical reactions of the conversion of metal sulphide to oxides can be performed on the basis of ΔG° and K values. These enable to assess the thermodynamic reaction ability order.
- Equilibrium composition of metal oxides after their conversion to oxides and subsequent assessment of thermodynamic efficiency give quantitative characteristics of the chemical reaction processes. Hence, this allows quantitative chemical thermodynamics to be considered.
- The products obtained by oxidation leaching in NaOH solution will be the input for the reduction of metal oxides of Cu (Sb, Bi, As, Hg). Following the thermodynamic process, Cu is obtained by the reduction in solid form. The reduction process is managed so as to reduce oxides of Cu without Fe.

- Conversion of metal sulphides to oxides makes it possible to produce non-ferrous metals without polluting the environment with sulphur and its oxides or compounds.
- Sulphur can be eventually obtained in the solid phase in the form of sulphate as a marketable product.

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